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PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Organometallic Compounds

- We, ETHYL CORPORATION, a corporation organised under the laws of the State of Delaware, United States of America, of 100, Park Avenue, New York 17, State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- This invention relates to a novel class of organometallic compounds and methods for their preparation.
- According to the present invention we provide new organometallic compounds having the formula $AMQ(Y)_n$, wherein M is a central metal atom which has an atomic number of from 7 to 14 less than that of the next higher rare gas of atomic number 36, 54 or 86, A is an arene molecule coordinately linked to said metal atom by donation of six electrons thereto, Q is at least one dissimilar electron donating group linked to said metal atom, each of which dissimilar groups donates from 1 to 8 electrons to said metal atom so that the electronic configuration of the said metal atom is equal to, or not more than two less than, the electronic configuration of the next higher rare gas, Y is an anion, and n has a value of 0 to 3.
- These novel compounds achieve stabilization through coordination of sufficient electrons to give the metal atom the electronic configuration similar to that of the next higher rare gas. The compounds of this invention can also be represented by the formula:
- $$AM(B)_b(C)_c(\gamma)_n$$
- wherein A, M, γ and n are defined above and B and C represent electron donating entities capable of donating from 1 to 8 electrons to the metal atom, b is an integer ranging from 1—8 and c is an integer ranging from 0—4, such that the atomic number of the metal M plus b times the number of electrons donated by B, plus c times the number of electrons donated by C plus n times the charge on γ plus the six electrons donated by the arene molecule A equals an integer having a value of from 34 to 36, 52 to 54, or 84 to 86, i.e. from two less than the atomic number of the next higher rare gas to the atomic number of the next higher rare gas, said rare gas having an atomic number of 36, 54 or 86 only.
- The central metal atom which is of atomic number 7 to 14 less than that of the next higher rare gas which has an atomic number of 36, 54 or 86, can be a metal of Group IVA—titanium, zirconium and hafnium; VA—vanadium, niobium and tantalum; VIA—chromium, molybdenum and tungsten; VIIA—manganese, technetium and rhenium; VIII—iron, ruthenium, osmium, cobalt, rhodium, iridium, nickel, palladium and platinum; and IB—copper, silver and gold.
- The arene molecule which is coordinated to the metal atom by donation of six electrons thereto can be any arene molecule although arene hydrocarbon molecules are preferred. Specifically, mono-nuclear hydrocarbons of 6 to 18 carbon atoms such as benzene, toluene, mesitylene, ethylbenzene and tetramethylbenzene, are preferred as components of the new cations. However, polynuclear hydrocarbons such as naphthalene can be used as can substituted hydrocarbons such as chlorobenzene and anisole.
- When an anion is present, the preferred anions of the new compounds are monovalent inorganic anions such as the halides—fluoride, chloride, bromide and iodide—the cyanide ion and the nitrate ion, although both organic anions and polyvalent inorganic anions are suitable.
- The constituents represented by B and C in the above formula are electron donating groups capable of coordinating with the metal atom in the novel compounds of this invention, and donating thereto from 1 to 8 electrons. That is, the groups represented by B and C in the above formula are capable of sharing electrons with the metal atom so that the metal achieves a more stable structure by virtue of such added electrons.

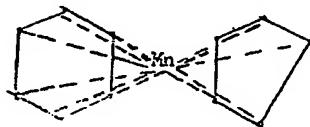
- These electron donating groups in coordination with the metal are either organic radicals or molecular species which contain labile electrons, which electrons assume a more stable configuration in the molecule when associated with the metal. The electron donating groups applicable to the compounds of this invention may also be inorganic entities which are also capable of existing as ions.
- Throughout this specification, the nomenclature of the compounds of this invention with respect to the electron donating groups is as follows. Those compounds containing groups which each share one electron with an electron from the metal atom thus forming a covalent bond therewith, are given names of the form "arene donor(s)-metal anion." Those compounds containing groups which donate from 2 to 8 electrons to the metal atom to form coordinate covalent bonds therewith, are given names of the form "arene metal donor(s) anion". When both types of donors are present the name given to the compound is of the form arene (1-electron)donor(s)-metal (2 to 8 electrons) donor(s) anion".
- Donors capable of sharing a single electron with a metal atom include monovalent organic radicals, the hydrogen atom, the cyanide group CN, and the halogens. These groups function as electron donors by sharing an electron with an electron of the metal atom in a single covalent bond. Examples of the arene metal coordination compounds of this invention which contain such a donor group include benzene dichloro-nickel and benzene tribromo-cobalt.
- Groups capable of sharing two electrons with a metal atom in the arene metal coordination compounds of this invention include mono olefins, ammonia, primary-, secondary-, and tertiary amines, cyclic nitrogen compounds wherein the nitrogen is in the trivalent state, organo phosphine compounds, phosphine halides, arsines, stibines, bismuthines, mixed hydroorganic phosphines, stibines, arsines and bismuthines, isonitriles and carbon monoxide. Examples of the compounds which contain such groups include benzene iron bis-triphenyl-phosphine, toluene methyl-cobalt pyridine, mesitylene cyano-cobalt arsine, butylbenzene nickel ethylene, benzene zirconium tetra-(methyl isonitrite), and toluene dimethyl-molybdenum diammonia.
- The nitrosyl group, NO, is an example of an entity capable of donating three electrons to a metal atom in the novel arene metal coordination compounds of this invention. Examples of these novel compounds which contain the nitrosyl coordination group include benzene cobalt nitrosyl, benzene manganese carbonyl nitrosyl, isopropylbenzene bromo-iron nitrosyl, and benzene cobalt nitrosyl.
- In the novel arene metal coordination compounds of this invention certain groups are capable of sharing four electrons in coordinate covalent bonds with the metal atom. These four electron donor groups include organic diamines, aliphatic diolefins, cyclic diolefins particularly those having conjugated double bonds, although non-conjugated cyclic diolefins are also applicable. When the donor group is a diamine best results are obtained when the methylene chain connecting the two nitrogen atoms is no longer than three carbons in length. Typical examples of the arene metal coordination compounds of this invention which contain stabilizing groups donating four electrons include ethylbenzene osmium dimethylene diamine, benzene hydro-manganese butadiene, toluene methyl-manganese N,N'-diphenyl methylene diamine, and toluene iron cyclohexadiene.
- The cyclopentadienyl radical contributes five electrons to certain of the novel arene metal coordination compounds of this invention. The cyclopentadienyl radical found in these novel compounds contains from 5 to 13 carbon atoms and thus includes the substituted cyclopentadienyl hydrocarbon radicals having up to 8 carbon atoms in a side chain substituent which may be bonded to more than 1 ring carbon atom. Examples of such radicals include the octylcyclopentadienyl radical, the methylcyclopentadienyl radical, and the indenyl radical. Examples of the novel coordination compounds of this invention containing such a cyclopentadienyl radical include benzene manganese cyclopentadienyl, toluene rhodium cyclopentadienyl and mesitylene manganese octylcyclopentadienyl.
- The cyclopentadienyl radical may also function as a monovalent organic radical in our compounds. Thus instead of being bonded to the metal atom in coordinate covalency through the carbon atoms of the cyclopentadienyl ring, the cyclopentadienyl group is bonded by a simple covalent bond to the metal atom. Typical examples of compounds containing the cyclopentadienyl group as a monovalent organic radical are benzene cyclopentadienyl-nickel and mesitylene di(ethylcyclopentadienyl)-cobalt.
- Aliphatic trienes represent entities capable of contributing six electrons to the metal in the arene metal coordination compounds of this invention. For this purpose compounds containing the three double bonds in conjugated relationship are preferred. Toluene tungsten hexatriene and benzene chlorotantalum 3-methylhexatriene are examples of arene metal coordination compounds stabilized by a conjugated triene electron donor group.
- The novel arene metal coordination compounds of this invention may contain a cycloheptatrienyl radical which contributes seven electrons in coordinate covalent bonding to the metal. The cycloheptatrienyl radical may be substituted with other hydrocarbon groups, and may contain a total of up to 15 carbon atoms. Examples of the arene metal coordination compounds of this invention which contain such cycloheptatrienyl radicals include benzene

vanadium cycloheptatrienyl, toluene zirconium methylcycloheptatrienyl, mesitylene chlorotitanium ethylcycloheptatrienyl and benzene methyl-zirconium octyl cycloheptatrienyl.

5 Tetraenes and in particular cyclooctatetraene may also be present in the arene metal coordination compounds of Group IVA. These tetraenes contribute 8 electrons in coordinate covalent bond with the metal. Such arene metal tetraene compounds are exemplified by benzene titanium cyclooctatetraene.

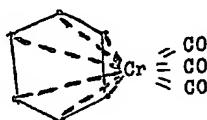
10 The number and nature of the dissimilar electron donating groups are always chosen so that the electronic configuration of the central metal atom of the cation is equal to or not more than two less than that of the next higher rare gas. In other words, the cations of the new compounds are made up of a combination of central metal atoms, coordinated molecules 15 and dissimilar electron donating groups so that the metal atom has either the electron structure of the next higher rare gas or is one or two electrons short of the configuration of the next higher rare gas. This critical electronic 20 configuration is an essential feature of our new compounds and appears to play a key role in their usefulness.

25 The compounds of this invention are quite different from any compound heretofore known. 30 The aromatic portion of the compound is actually an arene molecule, as distinguished from an aryl radical, e.g., phenyl, which is found in organo-metallic compounds. The arene molecule is not bonded to the metal 35 through a single carbon atom, as in the usual aryl metal compounds but, instead, each carbon of the aromatic ring is bonded apparently by coordinate covalency in a fashion such that the ring contributes six electrons to the metal atom. Likewise, the other electron donor groups 40 also are covalently or coordinatively bonded to the metal atom. Such donation of electrons contributes materially to the stability of the molecule since the metal atom, with the 45 donated electrons, approaches the electronic configuration of the next higher rare gas. In a preferred embodiment of this invention the metal atom has the electronic configuration of the next higher rare gas. For example, the 50 manganese atom in benzene manganese cyclopentadienyl has the electronic configuration of krypton. Thus in the case of benzene manganese cyclopentadienyl, the cyclopentadienyl group donates five electrons and the benzene molecule donates six electrons, giving a stable 55 compound which can be illustrated as follows:



In another, the chromium atom in benzene chromium tricarbonyl has the electron con-

figuration of krypton. Thus, in the case of benzene chromium tricarbonyl, the three CO groups donate a total of six electrons and the benzene molecule donates six electrons, giving a stable compound which can be illustrated as follows:



The novel compounds of this invention can be prepared by several methods. One of these 60 comprises the preparation of a diene metal complex followed by subsequent replacement of an arene molecule with an electron donating entity or entities. This may be accomplished in a single step or through a plurality of steps 65 which include the preparation of an arene metal coordination compound in which the arene-metal-ligand portion of the molecule exists as a cationic coordination compound of this invention. This may then be reduced to a neutral compound of this invention. In other cases the reaction product derived from replacing an arene molecule of a diene metal complex is a neutral coordination compound of this invention which is obtained without further reduction of the metal. In other instances the novel compounds of this invention are conveniently prepared by introducing an arene molecule in coordinate covalent bonding in a metal coordination compound such as a metal carbonyl derivative. The resulting intermediate may be an ionic compound which can be converted into a neutral compound.

Another method for the preparation of the 70 compounds of this invention consists of introducing into a metal compound an arene molecule. This may be done with the arene compound directly, or by means of an appropriate reagent such as a phenyl Grignard and subsequently converting the resulting complex to the neutral arene metal coordination compound desired. For example benzene manganese-cyclopentadienyl is prepared by treating a cyclopentadienyl manganese compound with excess phenyl Grignard and subsequently hydrolyzing the phenyl Grignard complex to the neutral benzene manganese cyclopentadienyl.

Ionic compounds of this invention are 75 conveniently prepared by reacting a compound of the central metal atom—frequently an inorganic compound—with an arene hydrocarbon which is to be coordinated with the central metal in the presence of a Lewis Acid material and usually also in the presence of the dissimilar electron donor. An example of this is reaction of molybdenum bromide with benzene and carbon monoxide in the presence of aluminum bromide to prepare benzene molybdenum tricarbonyl bromide. In some instances the 80 reaction between the source of the central 85

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- metal atom and the arene hydrocarbon is carried out first as a discrete step and the complex obtained thereby is further reacted with a source of a dissimilar electron donating group. 5 An example of this is reaction of molybdenum hexacarbonyl with benzene and aluminium bromide and reacting the intermediate thus produced with carbon monoxide to produce benzene molybdenum tricarbonyl bromide. A 10 further variation in production of the above compounds comprises reacting a compound of the desired metal, which compound already contains the dissimilar electron donor group or groups with the desired arene molecule in the presence of the Lewis acid catalyst. Such a process is typified by reaction of chloromanganese pentacarbonyl with toluene in the presence of aluminium chloride to produce toluene manganese tricarbonyl chloride. 15 20 The Lewis acid materials are the metal halides of the Friedel-Crafts type, notably the
- Analysis: Calculated for $C_{12}H_{12}O_5MnI$: C 37.4, H 3.12, Mn 14.2, I 32.9
Found: C 37.6, H 3.09, Mn 14.6, I 33.1
- EXAMPLE II. 45 A mixture of 10 parts of bromomanganese carbonyl, 5 parts of aluminium chloride and 130 parts toluene was refluxed for five hours under an inert atmosphere. After cooling, the 50 mixture was hydrolyzed with 80 parts of water,
- Analysis: Calculated for $C_{10}H_8MnO_3I$: C 33.6, H 2.25, Mn 15.4, I 35.6
Found: C 33.58, H 2.23, Mn 16.0, I 36.0
- In a similar run using the same conditions but with slightly varying reactant proportions a 94.5 per cent yield of the same product was obtained. 60
- EXAMPLE III. 65 Cobalt carbonyl is reacted with benzene in the presence of aluminium chloride to produce as an intermediate benzene cobalt carbonyl chloride. Without isolation this intermediate is reacted with nitric oxide under elevated pressure to produce as the final product benzene cobalt nitrosyl chloride.
- Analysis: Calculated for C_8H_6FeI : C 45.8, H 4.6, Fe 15.2
Found: C 45.6, H 4.73, Fe 15.0
- EXAMPLE V. 75 Titanium tetrachloride is reacted with phenyl magnesium bromide under Grignard conditions to produce diphenyl titanium dibromide. This intermediate when treated with carbon monoxide under pressure and in the presence of metallic copper gives benzene titanium tetracarbonyl. 90 Other typical ionic compounds of this invention include mesitylene nickel nitrosyl nitrate, toluene iron cyclopentadienyl nitrate, benzene dihydro-chromium cyclopentadienyl chloride, toluene vanadium tetracarbonyl fluoride, toluene tetracyano-zirconium dicar-
- anhydrous aluminium halides. The Friedel-Crafts catalyst is a salt having strong electrophilic characteristics. It can be any halide of a metal of Groups IIA, IIB, IIIB, IVA, VA, VIA, VIIA, and VIII of the Periodic Table. The halides of Groups IIB, IIIB, IVA and VIII are preferred. 25
- The following examples, in which all parts are by weight, more fully illustrate preparation of typical compounds of the invention. 30
- EXAMPLE I. 35 Bromomanganese pentacarbonyl was reacted with mesitylene under reflux in the presence of aluminium chloride, under a nitrogen atmosphere. Substantial amounts of a gas were evolved. Upon cessation of gas evolution the mixture was hydrolyzed with water. Upon saturating the water solution with potassium iodide, the product, mesitylene manganese tricarbonyl iodide, crystallized as ivory colored crystals in 90 per cent yield. 40
- EXAMPLE II. 45 A mixture of 10 parts of bromomanganese carbonyl, 5 parts of aluminium chloride and 130 parts toluene was refluxed for five hours under an inert atmosphere. After cooling, the 50 mixture was hydrolyzed with 80 parts of water,
- Analysis: Calculated for $C_{10}H_8MnO_3I$: C 33.6, H 2.25, Mn 15.4, I 35.6
Found: C 33.58, H 2.23, Mn 16.0, I 36.0
- Cyclopentadienyl iron dicarbonyl chloride (20 parts) was heated with 15 parts of aluminium chloride and 430 parts of mesitylene for 3 hours at 165° C. During the course of reaction a gas was given off and a dark liquid layer formed at the bottom of the reactor. At the end of the reaction period the mixture was cooled, hydrolyzed with 200 parts of water, filtered and the yellow water layer separated. The desired mesitylene iron cyclopentadienyl iodide was recovered from this aqueous layer in 40 per cent yield by precipitation with potassium iodide. 70
- EXAMPLE IV. 75
- bonyl iodide, ethylbenzene manganese nitrosyl dicarbonyl sulfate, benzene cobalt dicarbonyl iodide, chlorobenzene manganese tris-(trichlorophosphine)chloride, benzene chlorocopper chloride, chlorobenzene methyl-cobalt carbonyl iodide, triethylbenzene rhodium nitrosyl carbonyl cyanide, xylene tantalum nitrosyl diammonia iodide, benzene vanadium cyclopentadienyl carbonyl bromide, benzene chromium tricarbonyl nitrate, benzene rhodium nitrosyl fluoride, benzene nickel carbonyl iodide, benzene manganese cyclopentadienyl iodide and anisole dimethyl-palladium iodide. 100 105 110

EXAMPLE VI.

One hundred and twelve parts of bis-methylcyclopentadienyl manganese in 400 parts of tetrahydrofuran were added to 52 parts of manganese chloride in a vessel provided with stirring means and refluxing means. An atmosphere of nitrogen was maintained. The mixture was brought to reflux for 15 minutes and then cooled to room temperature. The resulting 5 methylcyclopentadienyl manganese chloride was not isolated. To this was added 360 parts of phenyl magnesium bromide dissolved in 1500 parts of tetrahydrofuran. This mixture was stirred with reflux overnight. The mixture 10 was then hydrolyzed with excess five per cent hydrochloric acid. The resulting organic layer was separated from the water later and evaporated at reduced pressure. Two hundred and fifty parts of benzene were added to the residues and evaporation again effected to remove water. The residues were then dissolved in 200 parts of petroleum ether, boiling point 15 35-45° C., and passed through a chromatographic column containing alumina. The material was eluted from the column with low-boiling petroleum ether and the product collected was a red solution. The solution was evaporated to give a pink solid, which on sublimation at reduced pressure gave mixed crystals, white 20 and red in color. The red and white crystals were then separated. The white crystals were diphenyl and the red crystals were benzene manganese methylcyclopentadienyl. These were purified further by subliming two more times. 25 The elemental analysis for the red crystals was 67.9 per cent carbon, 6.23 per cent hydrogen, and 25.9 per cent manganese. This corresponds very closely to the calculated analysis for benzene manganese methylcyclopentadienyl. The infrared spectrum completely supported the structure. Thermal decomposition of the benzene manganese methylcyclopentadienyl gave benzene in a 48 per cent of theoretical yield. The melting point of the 30 compound was 116-118° C.

A preferred preparative embodiment of the present invention is illustrated by the above example for the preparation of benzene manganese methylcyclopentadienyl. In general, this preferred embodiment comprises reacting a cyclopentadienyl metal compound, the metal being one of Groups IVA, VA, VIA, VIIA and VIII, with an aryl compound of a metal of Groups IA, IIA, IIIA, and IIIB under reducing conditions. This reaction product is decomposed to form the mono-metal arene metal cyclopentadienyl compound. This decomposition of the complex is normally accomplished by reaction with a compound having an active 35 hydrogen, e.g., hydrolysis or alcoholysis. The process is preferably conducted in an inert solvent, particularly an ether, polyether, acetal, or a tertiary amine.

A particularly preferred embodiment of this process comprises the reaction of a cyclopenta-

dienyl manganese compound with a phenyl Grignard reagent employing an excess of the Grignard reagent as a reducing component. The intermediate which results in this reaction is then hydrolyzed under mildly acid conditions to produce a benzene manganese cyclopentadienyl compound.

The aryl metal reactant has the aryl constituent bonded through a single carbon atom directly to the metal atom. The aryl metal compound can have one or more aryl constituents as in the case of phenyl sodium, diphenyl calcium, and triphenyl aluminium. Moreover, the polyvalent metals can have other groups in the molecule, including inorganic or organic anions.

The cyclopentadienyl metal compound can be a bis(cyclopentadienyl) metal compound or a cyclopentadienyl metal compound having inorganic or organic radicals.

The reducing conditions of the process can be provided by the use of an excess of the arene compound used to complex the Group VIIA metal compound or the reducing conditions can be provided by the use of auxiliary reducing media, in addition to the arene metal compound. When an auxiliary reducing medium is employed, it can be gaseous hydrogen, an active metal, a metal hydride, or an alkyl metal, particularly metals or metal compounds of Groups I-III of the Periodic Table. The preferred reducing media are soluble in the reaction system.

The auxiliary reducing medium can be employed for any of the metals in a wide range of concentrations, but especially preferred for use in preparing manganese compounds, e.g., from 0.1 to 5 moles per mole of manganous salt. Usually it is employed in about mole equivalent quantities.

The temperature of the process of this invention is not critical but usually is from about -50 to 200° C. and preferably between about 50-150° C.

The above process may be conducted at about atmospheric pressure, although in some cases subatmospheric or elevated pressures are desirable. Frequently, it is desired to employ the autogenous pressure of the system. When hydrogen is employed, a hydrogen partial pressure of from 1 to 100 atmospheres is suitable, preferably 10 to 100 atmospheres.

The ether solvents suitable in the present invention can be either mono- or polyethers. Typical examples of suitable ethers are dimethyl ether, methyl isopropyl ether, or mixtures of ethers. The preferred polyethers are ethylene glycol diethers, and cyclic ethers, such as dioxane and tetrahydrofuran.

The quantity of solvent employed in the process is not critical.

Typical examples of other arene manganese cyclopentadienyl compounds that can be readily prepared in accordance with the above process are benzoic acid manganese cyclopenta-

dienyl, cyanobenzene manganese methylcyclopentadienyl phenol manganese methylcyclopentadienyl, benzaldehyde manganese cyclopentadienyl. However, preferred compounds of this invention are those in which the arene portion of the compound is a hydrocarbon group.

EXAMPLE VII.

Example VI was repeated except that greenish mesityl magnesium bromide was employed instead of the phenyl derivative and the product was the orange, crystalline solid, mesitylene manganese methylcyclopentadienyl.

EXAMPLE VIII.

To seven parts of methylcyclopentadienyl manganese chloride was added seven parts of ethyl magnesium bromide as an auxiliary reducing medium. This was followed by the addition of ten parts of phenyl magnesium bromide and the mixture allowed to come up to room temperature with stirring. A gas was slowly evolved. The mixture was then refluxed for three hours, cooled to room temperature, and hydrolyzed with excess five per cent hydrochloric acid. The organic layer was separated, evaporated, and the product recovery of the benzene manganese methylcyclopentadienyl was the same as that outlined in Example VIII.

EXAMPLE IX.

The procedure of Example VI was followed except that 11.8 parts of bis-methylcyclopentadienyl manganese were reacted directly with 24 parts of phenyl magnesium bromide. The product recovery procedure was the same. A higher yield of benzene manganese methylcyclopentadienyl resulted.

In another run the procedure outlined in Example VI was followed except that seven parts of methylcyclopentadienyl manganese chloride were added to 30 parts of phenyl magnesium bromide.

Typical specific examples of compounds of this invention are benzene manganese methylcyclopentadienyl; benzene manganese dimethylcyclopentadienyl; and other benzene manganese cyclopentadienyl derivatives including ethylcyclopentadienyl; benzylcyclopentadienyl; *n*-octylcyclopentadienyl; phenylcyclopentadienyl; *p*-xylene manganese methylcyclopentadienyl; mesitylene manganese methylcyclopentadienyl; and toluene manganese indenyl.

Other examples of group VIIA aromatic coordination compounds of this invention include benzene chloro-manganese dicarbonyl; toluene dicyano-manganese nitrosyl; phenylbenzene isobutyl-manganese dicarbonyl; hexamethylbenzene pentacyano-rhenium; mesitylene manganese methylcyclopentadienyl; benzene manganese cyclopentadienyl; toluene manganese methylcyclopentadienyl; diphenyl manganese dimethylcyclopentadienyl; allylbenzene manganese nitrosyl tribromophosphine

and *n*-butylbenzene ethyl-manganese dicarbonyl.

EXAMPLE X.

Mesitylene manganese tricarbonyl iodide (3.86 parts) was dissolved in 100 parts of hot water and, while boiling, 3 parts of potassium cyanide were added. Mesitylene cyano-manganese dicarbonyl, a yellow precipitate, was formed directly, carbon monoxide being evolved in about one mole equivalent quantities. The reaction mixture was cooled and filtered and 2.26 parts of mesitylene cyano-manganese dicarbonyl product was obtained. This product was recrystallized in water three times, washed with a small amount of diethyl ether and dried under reduced pressure. The melting point of the mesitylene cyano-manganese dicarbonyl was 170-172° C. Chemical analysis of the product was as follows:

	Found	Calculated	85
Carbon	55.8	56.0	
Hydrogen	4.79	4.65	
Nitrogen	5.45	5.45	

An infrared spectrum confirmed the structure of this product. The product obtained in this example is an effective antiknock agent when used in fuels for internal combustion engines.

Example X is illustrative of another preferred preparative embodiment of this invention which in general comprises preparing arene cyano-manganese dicarbonyl compound by pyrolysis of an arene compound containing the arene manganese tricarbonyl cation in the presence of excess cyanide. The excess cyanide is preferably present in the form of an alkali metal or alkaline earth metal cyanide. A variant in this process comprises the pyrolysis of an arene manganese tricarbonyl cyanide to form the desired arene cyano-manganese dicarbonyl. This pyrolysis can be conducted at a temperature of between about 20° and 300° C., but is usually carried out between about 50° and 200° C. Likewise, while not essential, the reaction is best conducted in an inert liquid medium and preferably in a solvent for the tricarbonyl reactant but which is not a solvent for the product. For this reason, polar solvents are frequently preferred.

The pyrolysis to form the arene cyano-manganese dicarbonyl can be accomplished simultaneously with the formation of the arene manganese tricarbonyl cyanide reactant. For example, a typical method for producing the arene manganese tricarbonyl cyanide involves the reaction of an arene manganese tricarbonyl halide with an active cyanide compound. This reaction can be conducted at temperatures defined above for pyrolysis, i.e., 20-300° C., to simultaneously produce the compounds of this invention. Likewise, the arene manganese tricarbonyl halide does not require isolation prior to conversion to the compounds of the present invention.

EXAMPLE XI.

Mesitylene manganese tricarbonyl iodide (3.86 parts) was reacted with 2 parts of potassium cyanide, but in this example the iodide compound was dissolved in 150 parts of ice-cold water. A white precipitate was formed immediately which was thereafter filtered and washed with ethyl ether. This white precipitate, mesitylene manganese tricarbonyl cyanide, (2.45 parts) was analyzed by chemical analysis and by infrared analysis. This product was thereafter refluxed under nitrogen, resulting in the evolution of carbon monoxide. Upon cooling, yellow crystals separated which were thereafter recrystallized from water to give mesitylene cyano-manganese dicarbonyl having a melting point of 171-172° C.

EXAMPLE XII.

Mesitylene manganese tricarbonyl bromide in excess mesitylene and 100 parts of water was treated with excess potassium cyanide. A green precipitate was formed. Thereafter sufficient sodium hydroxide (5 per cent solution) was added to the reaction product to raise the pH to 8.5. The product was then extracted with water and the extract was concentrated to yield yellow crystals. Recrystallization from water gave 6.12 parts of mesitylene cyano-manganese dicarbonyl.

The Friedel-Crafts reaction is preferably carried out in a liquid medium consisting primarily of the arene compound which is reacted with the manganese pentacarbonyl reactant. The reaction can also be conducted in a halogenated benzene such as chlorobenzene or bromobenzene, in which event the chloro-arene or bromo-arene manganese tricarbonyl halide is formed. Other substituted arene compounds can be produced in like manner. In addition to the arene compound, diluents can be employed. Typical examples of such diluents are nitrobenzene; straight chain hydrocarbons such as pentane, hexane and decane.

Reaction of the arene manganese tricarbonyl halide with an active cyanide compound is best conducted at temperatures of from -30° to 250° C. Most preferred operation employs temperatures of above 50° C. and below about 200° C. At the more elevated temperatures, the arene manganese tricarbonyl cyanide decomposes immediately to the desired arene cyano-manganese dicarbonyl. In this process, any active cyanide compound can be used but the cyanides of metals of Groups I to III of the Periodic Table are preferred. Best results are obtained with the alkali metal compounds.

Any of a wide variety of solvents particularly polar solvents can be employed in the pyrolysis. Water, lower aliphatic alcohols and ethers such as acetone are preferred.

EXAMPLE XIII.

Iron carbonyl, benzene and aluminium chloride are reacted at the reflux temperature of the system with the evolution of carbon monoxide. The amounts of reactants employed

are as follows: iron carbonyl, 200 parts; benzene, 360 parts; aluminium chloride, 135 parts. Benzene iron dicarbonyl having the formula $C_6H_6Fe(CO)_2$ results from this reaction.

EXAMPLE XIV.

Dicobalt octacarbonyl, aluminium chloride and mesitylene are reacted according to the procedure of Example XIII to produce a good yield of the mesitylene cobaltate (I) dicarbonyl ion. This water soluble compound when treated with excess potassium cyanide and pyrolyzed, produces a good yield of mesitylene cyano-cobalt carbonyl, $(CH_3)_3C_6H_6Co(CO)CN$.

EXAMPLE XV.

To a glass reaction vessel equipped with stirring means, heating means and reflux condenser were added 35 parts of chromium hexacarbonyl and 430 parts of mesitylene, the excess as a carrier. The mixture was agitated and heated to reflux for 3 hours during which time gas evolved and was collected. The quantity of gas evolved corresponded to three equivalents of carbon monoxide. After discontinuing the heating and refluxing the reaction mixture was cooled. To recover the mesitylene chromium tricarbonyl from this solution the mesitylene is evaporated and the residue carefully sublimed. The mesitylene chromium tricarbonyl is insoluble in water but soluble in organic solvents and is oxidatively and thermally stable at temperatures in excess of its melting point which is above about 110° C.

Other Group VIA metal compounds of this invention are toluene chromium tricarbonyl; ethylbenzene chromium dinitrosyl; toluene cyano-chromium cyclopentadienyl; mesitylene bromo-chromium methylcyclopentadienyl; *p*-methyl diphenyl cyano-chromium octylcyclopentadienyl, ethylbenzene chromium triammonia; hexamethylbenzene phenyl-molybdenum cyclopentadienyl; toluene molybdenum tri-(dodecylamine); and benzene tungsten tri-(phenyl) isonitrile.

EXAMPLE XVI.

Methylcyclopentadienyl bromo-chromium tricarbonyl (300 parts), 850 parts of toluene and 180 parts of ferric chloride are heated to reflux over a period of six hours with constant agitation. During this heating an amount of gas is given off corresponding to the total amount of carbon monoxide in the carbon compound. After the reaction vessel is cooled the contents are hydrolyzed with 80 parts of weakly acidified water and the organic layer is separated. Toluene bromo-chromium methylcyclopentadienyl is separated in good yield from the organic layer. The methylcyclopentadienyl bromo-chromium tricarbonyl employed in this example is prepared by first treating chromium carbonyl with methylcyclopentadienyl sodium and then adding $HgCl_2$. The resulting salt is brominated to give the methylcyclopentadienyl bromo-chromium tricarbonyl.

Further examples of Group VIA arene co-

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- ordination compounds of this invention include *n*-butyl-benzene molybdenum tricarbonyl; *sec*-butylbenzene tungsten triammonia; and benzene molybdenum carbonyl trimethylene-diamine.
- Still other examples of Group VIA compounds of this invention include benzene chloro-chromium cyclopentadienyl; mesitylene cyano-chromium methylcyclopentadienyl; *o*-xylene hydro-chromium ethylcyclopentadienyl; cumene chromium dinitrosyl; isopropylbenzene chromium tris-(di-propylamine); durene chromium cyclopentadienyl; benzene chromium carbonyl nitrosyl; toluene chromium cyclopentadienyl; mesitylene chromium methylcyclopentadienyl; *o*-xylene chromium ethylcyclopentadienyl; ethylbenzene molybdenum *n*-octylcyclopentadienyl; diphenyl molybdenum diethylcyclopentadienyl; *n*-butylbenzene tungsten indenyl; and 1,2,3-triethylbenzene chromium ethylcyclopentadienyl.
- EXAMPLE XVII.**
- Working in a nitrogen atmosphere, 120 parts of titanium dichloride, 290 parts of aluminium tribromide and 1000 parts of ethylbenzene are refluxed for 4 hours. While the nitrogen atmosphere is maintained the reaction mixture is hydrolyzed with water and the organic layer containing di(ethylbenzene) titanium is then transferred while under nitrogen to a pressure resistant vessel. The vessel is sealed and pressurised with carbon monoxide to a pressure of about 500 psig. and the temperature is elevated to about 165° C. These conditions are maintained for about 3 hours after which time the pressure is vented, the vessel is discharged the contents subjected to fractional distillation at reduced pressure. Ethylbenzene titanium tetracarbonyl having the formula $C_6H_5C_6H_5Ti(CO)_4$ results.
- EXAMPLE XVIII.**
- To a solution of 1 mole of sodium cyclopentadienide (prepared from cyclopentadiene and sodium in tetrahydrofuran) was added dropwise under cooling 0.25 mole vanadium chloride. The solution was blanketed with nitrogen. The reaction is very violent, due in part to the complexing of the vanadium chloride with tetrahydrofuran. A dark reddish-purple solution resulted. This solution was charged to an autoclave and treated with carbon monoxide at a temperature of 175° C. and a pressure of 3000 psi CO for 1 hour. After cooling the reaction mixture was discharged, the solvent evaporated under nitrogen, and the cyclopentadienyl vanadium tetracarbonyl product was sublimed in high vacuum at 70—80° C. The sublimate was obtained as golden orange crystals, volatile and hydrocarbon soluble, m.p. 138° C.
- This cyclopentadienyl vanadium tetracarbonyl (1.0 mole) is treated with 1.1 mole (a slight excess) of aluminium tribromide in the presence of a 10 fold excess of toluene.
- The mixture is refluxed for about 2 hours, and after hydrolysis and fractional distillation of the resulting organic layer, toluene vanadium cyclopentadienyl carbonyl is isolated and purified by recrystallization at reduced temperatures.
- Examples of other Group VA compounds of this invention include benzene vanadium methylcyclopentadienyl carbonyl; toluene dicyano-vanadium cyclopentadienyl; *p*-xylene vanadium butylcyclopentadienyl; mesitylene dibromo-vanadium dimethylcyclopentadienyl; cumene methyl-vanadium dinitrosyl; benzene ethyl-vanadium tricarbonyl; isopropylbenzene iodo-vanadium dinitrosyl; allylbenzene vanadium nitrosyl dicarbonyl; benzene chlorovanadium tris-(*tert*-phenylamine); toluene niobium methylenediamine nitrosyl; and hexamethylbenzene dodecyl-tantalum tricarbonyl.
- The novel arene metal compounds of this invention can be employed as polymerization catalysts in the polymerization of olefins; as drying agents in drying oil compositions and as metal sources in gas-phase plating operations. The Group IVA metals and particularly titanium compounds of this invention are preferred as polymerization catalysts. They are often employed together with aluminium and aluminium halides in the pressure polymerisation of such unsaturated compounds as ethylene. For use as dryers the zirconium and chromium compounds of this invention are preferred, whereas in gas plating operations the tantalum, chromium and tungsten compounds find the greatest utility as they produce higher acid resistance coatings on the surface to which they are bonded.
- The compounds of the present invention possess utility as agents improving the operation of the internal combustion engine. When the compounds are ionic it is preferred to inject the new compounds directly into the combustion chamber of the internal combustion engine as an aqueous solution or suspension. When injected into the chamber in such a fashion it is found that the new compounds exhibit potent antiknock activity and also provide important deposit modification effects.
- Some of our new compounds particularly those wherein the anion is composed of a long chain organic radical and those which are non-ionic are soluble in gasoline and can be used directly therein as a fuel additive.
- Another utility of the present compounds is as an intermediate in the production of fuel-soluble organic metallic compounds useful as antiknock agents. The following example typifies such a use.
- EXAMPLE XIX.**
- Two hundred parts of mesitylene manganese tricarbonyl iodide were dissolved in 5000 parts of potassium hydroxide solution under nitrogen atmosphere. To this solution was added 500 parts of cyclopentadiene and the mixture was refluxed for 10 minutes. After cooling, ether

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- was added and the mass was filtered with the use of a filter aid. The filtrate was evaporated and the oily residue sublimed at 60° under reduced pressure. From this sublimation was obtained cyclopentadienyl manganese tricarbonyl, melting point 75—76° as yellow crystals. The identity of this product was confirmed by infrared spectrum.
- Cyclopentadienyl manganese tricarbonyl compounds are known to be potent antiknocks agents when dissolved in gasoline.
- Other important uses of the ionic arene metal compounds of the present invention include the use thereof as chemical intermediates, particularly in the preparation of metal and metalloid containing polymeric materials. In addition, some of the compounds of this invention can be used in the manufacture of medicinals and other therapeutic materials, as well as agricultural chemicals such as, for example, fungicides, defoliants, and growth regulators.
- WHAT WE CLAIM IS:—**
1. An organometallic compound having the formula
$$\text{AMQ(Y)}_n$$
 wherein M is a central metal atom which has an atomic number of from 7 to 14 less than that of the next higher rare gas of atomic number 36, 54 or 86, A is an arene molecule coordinately linked to said metal atom by donation of 6 electrons thereto, Q is at least one dissimilar electron donating group linked to said metal atom each of which dissimilar group donates from 1 to 8 electrons to said metal atom so that the electronic configuration of the said metal atom is equal to or not more than two less than the electronic configuration of the next higher rare gas, Y is an anion, and n has a value of 0—3.
 2. A compound according to claim 1, wherein M represents a transition metal from Groups IV A, V A, VI A, VII A and VIII of the Periodic Table, and A represents an arene compound having a benzene nucleus.
 3. A compound according to claim 2, in which the group AMQ is ionic.
 4. A compound according to claim 3, wherein the electronic configuration of the said metal atom M is equal to or one less than the electronic configuration of the next higher rare gas.
 5. An ionic arene coordination compound of manganese wherein an arene molecule is coordinately bonded to manganese, said compound comprising an arene manganese tricarbonyl cation and an anion.
 6. An arene manganese tricarbonyl halide.
 7. An ionic arene coordination compound of iron wherein an arene molecule is coordinately bonded to iron, said compound comprising an arene iron cyclopentadienyl cation and an anion.
 8. An arene iron cyclopentadienyl halide.
 9. A compound according to claim 2, where-
- in n is O and the group AMQ is non-ionic.
10. Benzene manganese methylcyclopenta-dienyl.
11. An arene manganese dicarbonyl cyanide coordination compound wherein the arene molecule is coordinately bonded to manganese and wherein manganese achieves the electronic configuration of krypton.
12. A compound according to claim 9, wherein M is a Group VIA metal and wherein said VIA metal achieves the electronic configuration of the next higher rare gas.
13. A compound according to claim 12, wherein the Group VIA metal is coordinated with three tricarbonyl groups.
14. A process for preparing an organometallic compound which consists of a central metal atom which has an atomic number of from 7 to 14 less than that of the next higher rare gas of atomic number 36, 54 or 86, a single arene molecule coordinately linked to said metal atom by donation of 6 electrons thereto, and at least one dissimilar electron donating group linked to said metal atom each of which dissimilar group donates from 1 to 8 electrons to said metal atom so that the electronic configuration of the said metal atom is equal to or not more than two less than the electronic configuration of the next higher rare gas, characterized by introducing an arene molecule in coordinated covalent bonding in a metal compound.
15. The process according to claim 14, wherein a cyclopentadienyl metal compound is reacted under reducing conditions with an arene compound of a metal of Groups I to III, in which the arene group is bonded directly through a single carbon atom to the Group I to III metal, at a temperature between about -50 and 200° C. and thereafter reacting the intermediate reaction product with active hydrogen, the metal in the cyclopentadienyl metal compound reaction having an electronic configuration equal to, or not more than two less than, the electronic configuration of the next higher rare gas of the Periodic Table.
16. The process according to claim 15, characterized by the fact that the intermediate reaction product is reacted with a Grignard reactant prior to reaction with active hydrogen.
17. A process for preparing an organometallic compound which consists of a central metal atom which has an atomic number of from 7 to 14 less than that of the next higher rare gas of atomic number 36, 54 or 86, a single arene molecule coordinately linked to said metal atom by donation of 6 electrons thereto, and at least one dissimilar electron donating group linked to said metal atom each of which dissimilar group donates from 1 to 8 electrons to said metal atom so that the electronic configuration of the said metal atom is equal to or not more than two less than the electronic configuration of the next higher rare gas.

higher rare gas characterized by introducing an arene molecule in coordinated covalent bonding in a metal coordination compound

18. The process for preparing a compound having the formula



wherein A represents an arene compound having a benzene nucleus coordinated to the metal atom M through carbon atoms of the benzene ring, Q represents two or more carbonyl groups, and Y represents an anion and n has a value from 0—3, which process comprises reacting a metal carbonyl or a metal carbonyl halide compound with an arene com-

pound in the presence of a Friedel-Crafts catalyst.

19. A process which comprises reacting an arene hydrocarbon compound with a manganese pentacarbonyl compound in the presence of a Friedel-Crafts catalyst.

20. A process for preparing organometallic compounds substantially as herein described.

21. Organometallic compounds when prepared by the process according to any one of claims 14—19.

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